# ACID MINE WATER CONTROL*

by

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## INTRODUCTION

The seriousness of water pollution by acid drainage from coal mines is highlighted by the following figures: In Appalachia during 1966, more than 6,000 tons of acidity per day were discharged from active and inactive mines, polluting more than 10,000 miles of streams (1). To find solutions to the complex problems of acid mine drainage pollution, the Federal Water Pollution Control Administration (FWPCA) of the U.S. Deptment of the Interior has launched a program to prevent and control this source of pollution.

FWPCA has initiated a broad research program which includes research by its own staff and by industry, universities, state agencies, and research firms, under research and development grants and contracts authorized by 1966 amendments to the Federal Water Pollution Control Act. A summary of all FWPCA mine drainage research and development projects was recently published (2).

The research currently under way can be divided into three broad categories: (1) mechanisms of pyrite oxidation and mine drainage chemistry, (2) methods for preventing the formation of mine drainage, and (3) methods for treating mine drainage. A review of the current status of each of these areas follows.

## MECHANISMS OF MINE DRAINAGE CHEMISTRY

Since the 1920's, various researchers have been attempting to determine the mechanisms involved in the production of mine drainage. In recent years, a concentrated effort has been made in this area.

It is generally agreed that the initial step in the production of acid is the oxidation of $FeS_2$ (pyrite) to release ferrous iron, sulfate and acid (equation a). The rate of this reaction is dependent on the properties and composition of the pyrite, temperature, pH of the environment, and oxygen concentration. Smith, et al.,(3) have demonstrated that

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the reaction rate increased with an increase in pH. Water was found to be a reaction medium rather than a reactant, and the oxidation rate was a function of relative saturation in vapor phase oxidation. The rate at 100 percent saturation was the same as in an aqueous phase oxidation at the same partial pressure of oxygen. The role, if any, that bacteria plays in these reactions has not been established. Baker and Wilshire(4) have also been studying the mechanism of pyrite oxidation.

(a) $FeS_2(S) + 7/2\ O_2 + H_2O = 2SO_4^{-2} + 2H^+ + Fe^{+2}$

Following the oxidation of pyrite, the ferrous iron is further oxidized to the ferric form as shown in equations (b) and (c).

(b) $Fe^{+2} + 1/4\ O_2 + H^+ = Fe^{+3} + 1/2\ H_2O$

(c) $2FeSO_4 + O = H_2SO_4 = Fe_2(SO_4)_3 + H_2O$

This reaction has received considerable attention in recent years.(5)(6)(7)(8) Stumm and Singer(8) found that, in "clean" chemical systems in the pH-region corresponding to conditions encountered in mine drainage waters, the reaction proceeds relatively slowly (t 50 of approximately 1,000 days) and is independent of pH. However, they found that micro-organisms; inorganic ligands, such as sulfate; soluble metal ions, such as copper (II), aluminum, and manganese (II); and suspended material with large surface areas and high absorption capacities, such as clay particles, catalyzed the oxidation of ferrous iron. Bacteria play a dominant role in the oxidation of ferrous iron and probably account for the rapid oxidation noted in mining environments.(9)

Once ferric iron is formed, it may be removed from the pyrite oxidation system through hydrolyses as shown in equation (c) and (d), or remain in the system and further oxidize pyrite as noted in equation (e).

(c) $Fe^{+3} + 3H_2O = Fe(OH)_3\ (s)\ 3H^+$

(d) $Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4$

(e) $FeS_2(s) + 14Fe^{+3} + 8H_2O = 15Fe^{+2} + 2SO_4^{-2} + 16H^+$

The hydrolysis of the ferric iron results in the formation of ferric sulfate, which readily precipitates at pH's greater than 4, and additional acid. Thus, the oxidation and hydrolysis of one mole of iron pyrite ultimately leads to four equivalents of acidity. Stumm and Singer have studied the kinetics of ferric iron hydrolysis.(8)

If ferrous iron is oxidized to ferric iron in the presence of pyrite, the ferric iron will react with the pyrite to release more ferrous iron and acid, as can be seen from equation (e). Many investigators (3)(8)(9) have demonstrated that the rate of pyrite oxidation by ferric iron is much higher than that by oxygen. Thus, pyrite can be oxidized without the presence of oxygen if a source of ferric iron is available.

In order for the ferric iron to be present, it must either be carried to the pyrite site by water movement within the mine environment or be formed on the pyrite site through the oxidation of ferrous iron. Both mechanisms probably occur; however, it would appear that the supply of ferric iron to the pyrite site would be greater in refuse piles and surface mine spoils than in the walls and roof of an underground mine.

Although our understanding of mine drainage chemistry has increased severalfold recently, there is still much to be learned. This basic knowledge must be applied to development of methods to prevent acid mine drainage.

## PREVENTION OF MINE DRAINAGE FORMATION

The ultimate mine drainage abatement procedure is the prevention of the formation of acid mine drainage. Several research projects are being developed along these lines as noted in the succeeding text.

### Surface Mines

The surface mining industry has long recognized that pollution from mine drainage can be reduced by the burial of spoil and refuse bearing pyrite, the permanent flooding of toxic material, the diversion of water from mining operations, the rapid removal of that water which gains access to the mining operation, by proper backfilling of worked-out pits to cover toxic material and facilitate rapid removal of water and by revegetation of areas distrubed by mining to prevent erosion. The major surface mining States currently have laws that require these pollution control measures and in most cases, the industry is adhering to them. Our success to date in acid drainage control from surface mining does not mean that we are not looking for new and better ways to work and reclaim surface mines to achieve even greater pollution control.

We still have the major problem of preventing pollution from the "prelaw" abandoned surface mines, refuse piles, and slurry ponds. The Department of Interior has reported that 2,040,600 acres of surface mines require reclamation at an estimated cost of 0.75 to 1.2 billion dollars.(10)

Method of reclaiming abandoned surface mines and refuse piles are being studied. FWPCA has awarded Truax-Traer Coal Company $490,560 to demonstrate various procedures for reclaiming refuse piles and slurry lagoons to eliminate acid drainage.(2) The Commonwealth of Pennsylvania has a number of projects under way to reclaim abandoned surface mines, for example, at Moraine State Park an estimated 459 acres of abandoned strip areas will be restored.(11) The remedial program calls for the use of contour and terrace backfills, soil treatment, diversion ditches, slope drain flumes, and revegetation. FWPCA will pay part of the cost to evaluate the effectiveness of these measures.(2)

The FWPCA has a project near Elkins, West Virginia, which was designed to demonstrate methods of reclaiming surface mines.(12)(13) More than 12.5 miles of surface mines were reclaimed at this site. The construction phase of this project was completed in 1967, and the area was revegetated in the spring of 1968. Although the water quality of streams draining the reclaimed mines did not show an immediate improvement, there has been a steady improvement since the reclamation was completed (Table I).

TABLE I

Effect of Surface Mine Reclamation in Watershed RT 8F-1

| | Acidity (Hot) $CaCO_3$ mg/l | pH | Iron Total mg/l | Sulfate mg/l |
|---|---|---|---|---|
| Before Reclamation (Mean) | 199 | 3.0[a] | 19 | 290 |
| Minimum Value | 73 | 3.4[b] | 4 | 140 |
| After Reclamation | | | | |
| Oct. 67 | 107 | 3.4 | 28 | 220 |
| Nov. 67 | 145 | 3.4 | 19 | 220 |
| Dec. 67 | 921[c] | 3.4 | 20 | 215 |
| Jan. 68 | 38 | 4.8 | 6 | 78 |
| Feb. 68 | 111 | 3.5 | 14 | 180 |
| March 68 | 95 | 3.3 | 17 | 190 |
| April 68 | 54 | 3.9 | 8 | 112 |
| May 68 | 71 | 3.8 | 14 | 140 |
| June 68 | 83 | 3.6 | 12 | 185 |
| July 68 | 27 | 4.1 | 0.8 | 190 |
| Aug. 68 | 135 | 3.5 | 13 | 175 |
| Sept. 68 | 89 | 3.5 | 10 | 150 |
| Oct. 68 | 55 | 3.7 | 8 | 155 |
| Nov. 68 | 37 | 4.1 | 3 | 135 |
| Dec. 68 | 94 | 3.5 | 9 | 220 |
| Jan. 69 | 567[d] | 3.3 | 37 | 290 |

a. Median value
b. Maximum value
c. A flush of mine drainage from underground mine occurred
d. High flow - possible flush from underground mine

## Underground Mines

The development of methods for preventing mine drainage pollution from underground mines is far more difficult than for surface mines. Preventing water from entering the mine, and the rapid removal of that

water which does enter the mine have been demonstrated as sound methods of reducing acid pollution. Permanent flooding of deep mine workings below drainage has also been found to prevent acid formation. Three projects currently underway will attempt to demonstrate that above-drainage underground mines can be flooded to reduce acid production. Halliburton Company has constructed a plug in a drift mine opening by filling a rubber retainer with grout.(2)(14) Approximately seven feet of head will develop behind the plug and flood the mine. They are also developing other types of bulkhead seals. At Moraine State Park, the Commonwealth of Pennsylvania (2)(15) is to hydraulically grout seal 53 drift mine openings and flood the mines. The most ambitious mine flooding project will be undertaken in the Catawissa Creek Watershed of Pennsylvania, where a large abandoned anthracite mine will be flooded.(2) Here, the head on the seal will be several hundred feet. In a separate study, but one closely aligned with the mine flooding projects, the insitu precipitation of sludge within a mine to seal leaky areas along the mine outcrop is being studied.(2) Work on flooding drift mines has just begun, and it will be several years before the effectiveness of this method will be known.

Air sealing, a popular practice since the early 1930's for preventing acid mine drainage pollution, has been the subject of considerable controversy. The method is based on the theory that if oxygen is excluded from the mine, the oxidation of pyrite (equation a) and ferrous iron (equation b) cannot occur or will be reduced. Shumate and Smith(16) found that acid production was decreased by only 40 to 50 percent when they decreased the oxygen concentration to less than two percent by pumping nitrogen into a mine. They also found that a significant lag time occurred between changes in environmental conditions associated with oxygen concentrations at the reactive site and reflection of these changes in mine drainage characteristics. Furthermore, they discovered that a significant amount of air entered a mine through the overburden because of barometric changes (breathing of mine).

The U. S. Bureau of Mines reported a decrease, but not elimination in the acid discharge from a sealed mine.(17) Building masonry air seals at all portals, and filling all other known openings into the mine resulted only in a decrease in oxygen content to 16 percent.

The FWPCA sealed a mine near Elkins, West Virginia.(13) Table II shows that the oxygen content in that mine was only reduced to 7.2 percent; however, some improvement occurred in the water quality.

TABLE II

Effectiveness of Mine Seal - Area 24

| | Oxygen[a] Within Mine, Percent | Acidity (Hot) $CaCO_3$ mg/l | pH | Iron, mg/l | Sulfate, mg/l |
|---|---|---|---|---|---|
| Before Sealing[b] (Mean) | ---- | 591 (65)[c] | 2.8[d] | 93(25)[c] | 1,035 (155)[c] |
| Minimum | ---- | 438 | 3.1[e] | 48 | 710 |
| After Sealing | | | | | |
| Oct. 67 | ---- | 388 | 3.1 | 86 | 835 |
| Nov. 67 | 9.1 | 365 | 3.2 | 83 | 770 |
| Dec. 67 | ---- | 325 | 3.2 | 87 | 785 |
| Jan. 68 | 7.8 | 315 | 3.1 | 75 | 655 |
| Feb. 68 | ---- | 328 | 3.2 | 69 | 700 |
| March 68 | 8.8 | 332 | 3.2 | 77 | 703 |
| April 68 | ---- | 277 | 3.3 | 60 | 625 |
| May 68 | 10.8 | 344 | 3.3 | 64 | 620 |
| June 68 | ---- | 382 | 3.0 | 81 | 860 |
| July 68 | 7.0 | 354 | 3.2 | 73 | 780 |
| Aug. 68 | ---- | 318 | 3.2 | 70 | 665 |
| Sept. 68 | ---- | 360 | 3.0 | 74 | 680 |
| Oct. 68 | 7.2 | 279 | 3.2 | 74 | 630 |
| Nov. 68 | 7.6 | 247 | 3.2 | 78 | 660 |
| Dec. 68 | ---- | 269 | 3.2 | 66 | 590 |
| Jan. 69 | ---- | 373 | 3.3 | 62 | 700 |

a. Data collected by U.S. Bureau of Mines
b. March 1964 - August 1967
c. Number in parenthesis is standard deviation
d. Median value
e. Maximum value

These studies demonstrate that acid production from underground mines can be reduced, but not eliminated, by air sealing. The major technological difficulty appears to be sealing the mine in such a way that no air can gain access. Masonry seals at the portals, and the plugging of other openings into the mine, cannot prevent air from entering in significant amounts. Air is forced in during barometric changes. In an attempt to overcome the "breathing" problem in a sealed mine, studies have been initiated on the effect of filling a mine with an inert gas and maintaining a slight positive pressure.(2)

Another preventive technique under study is the use of bacterial inhibiting agents (2) which could result in decreased acid production by reducing the rate of reactions described in equations (a) and (b). This study is still in the laboratory stage.

# TREATMENT OF MINE DRAINAGE

In many situations, the only positive acid mine drainage control technique available is treatment of the discharge. Treatment appears to be best suited to active mine operations, to abandoned mines where preventive measures are not applicable, and to residual pollution from preventive methods. A state-of-the-art report concerning mine drainage treatment has recently been published by FWPCA.(18)

## Neutralization

The Commonwealth of Pennsylvania has issued over 263 permits to mining companies for the construction of neutralization plants for mine drainage. All but a few of these plants use lime for the neutralization of the acidity. Where ferrous iron is a problem, aeration is used to convert ferrous iron to insoluble ferric hydroxide. The sludge produced by neutralization-aeration is removed either in a settling pond or basin and then disposed of in holding ponds or abandoned underground mines. Major problems with this type of system are the oxidation of the ferrous iron and the settling and disposal of large volumes of difficult-to-handle sludge. Lime neutralization-aeration is an effective process for increasing the pH; decreasing the acidity, iron, and aluminum; and removing some sulfate. The treated water still contains a high concentration of calcium, magnesium, and sulfate.

Several research projects are in progress to improve the neutralization-aeration process.(2) As part of this work, limestone, which is cheaper than lime and produces a faster settling and denser sludge, is under study. When sufficient reaction time is allowed, and when the limestone has a high calcium content, and is finely ground (less than 200 mesh) good results are obtained.

Bituminous Coal Research, Incorporated, has been investigating the use of sulfides to remove iron.(19) The iron is precipitated as ferric sulfide. Also under investigation are various methods for increasing the rate of ferrous iron oxidation, such as the use of catalysts.

## Biological Treatment

Bacteria may prove of great benefit in the treatment of mine drainage. Research has shown that bacteria increase the rate of ferrous iron oxidation. FWPCA has funded a study at Continental Oil Company to evaluate and demonstrate this process.(2) Dugan, et al.,(20) have demonstrated that under specific conditions bacteria can reduce sulfate to sulfide, resulting in an increase in pH, and a decrease in acidity and iron. Continental Oil Company and Syracuse University are studying this procedure further.(2)

## Other Treatment Methods

Neutralization-aeration treatment of mine drainage removes only part of the contaminates. If the treated water is to be used for industrial or domestic purposes, hardness and the sulfates must be removed. FWPCA, in cooperation with the Office of Saline Water of the U. S. Department of the Interior, has been evaluating the use of reverse osmosis for the treatment of mine drainage.(18) These studies show that reverse osmosis can produce a high-quality water. Disposal of concentrated brine material is a major problem.

Ion exchange also appears to have merit in the treatment of mine drainage.(18) A full-scale ion exchange plant will soon be constructed by the Commonwealth of Pennsylvania. A feasibility study on the use of the freezing process is also underway.(2)

A method is available today for the control of acid mine drainage-treatment. It is obvious that this is not the ideal method because it is a never ending process. However, until preventive methods of development, and demonstration, it will serve as our primary control measure. Effort must be placed on developing preventive methods for underground mines and abandoned surface mines.

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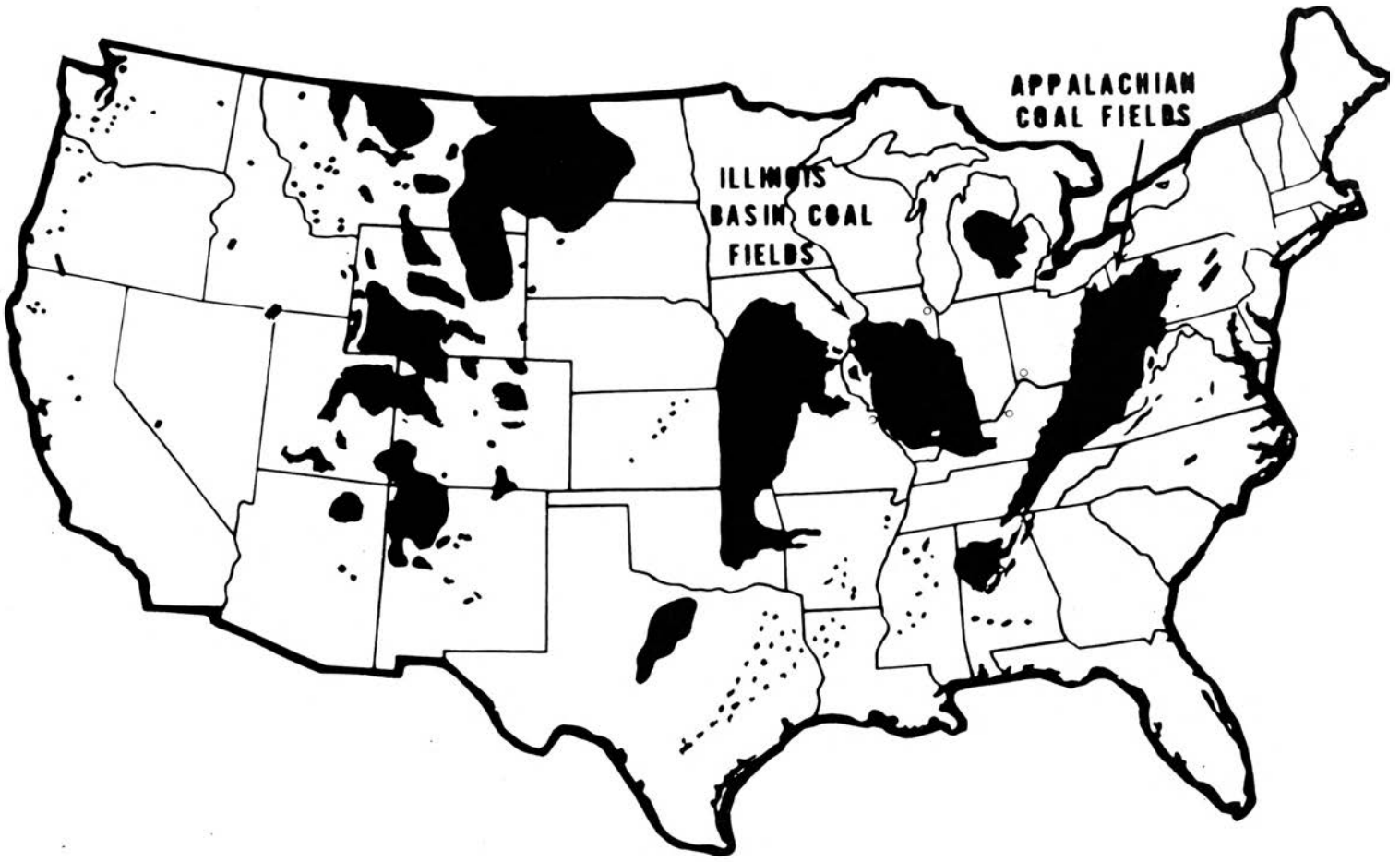


# FIGURE 1

## Coal Producing Areas in the United States

## COMMENTS

Mr. Cook: "I would like to throw a couple of dollars and cents into this picture because this is a part of the problem that is going to come up. We have 500 operating mines in the state of Ohio and that is only a drop in the bucket to what they have in Pennsylvania, West Virginia, and Kentucky. So you are talking about a large industry. There are a lot of abandoned operations. At the present time those are the obligation of the present land owner but let me give you an example of what happened in Illinois when Peabody Coal Co. bought an operation that had been there many years. They are now faced with the problem of going in there and taking care of the whole problem that they bought. They bought a problem; this problem will not be solved very cheaply. I know that in that area of the Saline River we found one operator that was in the process of covering abandoned spoil material or abandoned refuse material with material that was adjacent to it and available easily and that cost $17.00 an acre. In Perry County, Ohio we have just completed a project. This one involved some old underground workings that were there at the turn of the century and are bleeding down into more recently abandoned operations which were reclaimed, but in order to go in and do this job it is going to amount to about $900 an acre. And of course the controlling board in Ohio says, 'why in the world should we spend $900 an acre to go in and reclaim this when we have not got any land in this area any where near the amount in value.' They are doing it to protect other investments."